

Specific Heats of Fluorine at Coexistence*

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Experimental specific heats of fluorine at constant total volume are reported for the two-phase, liquid-vapor system from triple- to the critical point. Specific heats of liquid along the coexistence path are derived by use of PVT data for the two-phase system, and are represented by a formula to facilitate computations of thermodynamic properties.

Key words: Fluorine; liquid-vapor coexistence; saturated liquid; saturation; specific heats; thermodynamic properties; two-phase.

List of Symbols

| | |
|----------------------|--|
| A_i | coefficients for various formulas |
| C_o | gross heat capacity, adjusted for capillary tube |
| $C_b(T)$ | tare heat capacity of empty bomb |
| $C_v^0(T)$ | specific heat at $\rho = 0$ |
| $\bar{C}_v(\rho, T)$ | specific heat of two-phase sample |
| $C_\sigma(T)$ | specific heat of liquid on coexistence path |
| G | Gibbs free energy per mole |
| J | the joule |
| k | conversion factor, 101.325 J/liter atm |
| ℓ | the liter |
| N | total g moles of fluid in closed system |
| N_b | g moles of fluid in the bomb |
| N_c | g moles of fluid in the capillary tube |
| P | pressure, 1 MN/m ² = 9.86923 atm |
| Q | calorimetric heat input, J |
| ρ | density (subscripts g and l refer to vapor and liquid) |
| $\rho_{av} \equiv$ | N_b/V_b , overall density |
| T | temperature, K, on the IPTS (1968) |
| T_a | average temperature in ΔT |
| ΔT | calorimetric temperature increment, K |
| $v \equiv$ | 1/ ρ , molal volume |
| V_b | volume of the calorimeter bomb |

1. Introduction

These specific heat measurements are part of a program to determine thermodynamic properties of compressed gaseous and liquid fluorine [1, 2].¹ For computations of the thermodynamic properties of the

compressed liquid it may be convenient to use the saturated liquid path from the triple point to near the critical point. Data for specific heats of liquid on this path are derived from experimental observations on the two-phase, liquid-vapor system at constant volume by use of the PVT properties at coexistence.

2. Experimental Procedure

The commercial fluorine very generously was purified for us by G. K. Johnson at the Argonne National Laboratory by fractional distillation. Analyses of samples from our laboratory show a purity of at least 99.99 percent (determined by residual gas analysis after reaction of the fluorine with mercury). Most of the apparatus and procedures are identical with those described for our work on oxygen [3].

The fluorine sample-handling system is shown schematically by figure 1. The small circles represent valves. Numbers 8, 9, and 11 are packless valves, kindly given to us by G. C. Straty [4]. The pure fluorine is stored at 15 atm (1.5 MN/m²) pressure in the 10-liter, stainless steel tank. It is introduced to the calorimeter by condensing it first in the trap, cooled with liquid nitrogen. Pressures to 200 atm (20 MN/m²) are obtained in the calorimeter as the trap warms toward room temperature. The null-pressure diaphragm, NPD, isolates the fluorine from the remainder of the precision, dead-weight gage system. At the end of an experiment, fluorine is returned to the 10-liter storage vessel. Sodium fluoride pellets are activated by heating sodium bifluoride. They absorb traces of HF which could arise from organic contaminants in the all-metal system. The activated alumina converts fluorine into oxygen for protection of the rotary pump (containing fluorocarbon oils).

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¹ Figures in brackets indicate the literature references at the end of this paper.

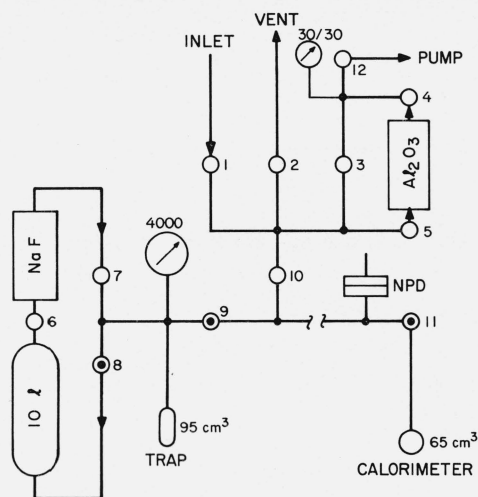


FIGURE 1. Fluorine sample-handling system.

Temperatures are on the IPTS (1968) via a new calibration table for our platinum resistance thermometer provided by the NBS temperature section [5]. To avoid entering a calibration table in the computer memory for every set of calculations, we have used a formula for computing temperature directly as a function of the observed thermometer resistance, as described in the appendix.

Tare heat capacity of the empty calorimeter bomb was measured in 29 intervals from 58 to 297 K. Data and the formulation are given in the appendix.

The amount of sample for each isochore of specific heat measurements is given in table 1. As in [3], we used an equation of state to find the density corresponding to the observed filling temperature and pressure. For present work the equation is similar to that used in [6], adjusted for forthcoming PVT data on fluorine.

3. Calculations and Results

Calculations in the present work differ from [3] only in modification of the heat of vaporization used for the capillary tube adjustment, as pointed out by R. E. Barieau in section 7 of [3]. With symbols listed above, the gross heat capacity, adjusted for heat effect of vapor forced into the capillary tube, is—

$$C_0 = [Q - T_a \cdot (dP/dT) \cdot \delta N_c / \rho_g] / \Delta T. \quad (1)$$

Specific heat of the two-phase sample, adjusted for heat effect of the bomb expansion, is—

$$\bar{C}_v = [C_0 - C_b - T_a \cdot (dP/dT) \cdot (dV_b/dT)] / N_b. \quad (2)$$

Physical properties needed for these calculations are given in the appendix.

Figure 2 locates the experimental runs by dashed lines inside the coexistence envelope. They represent the overall density of the two-phase system at constant volume. Table 2 gives the experimental conditions and

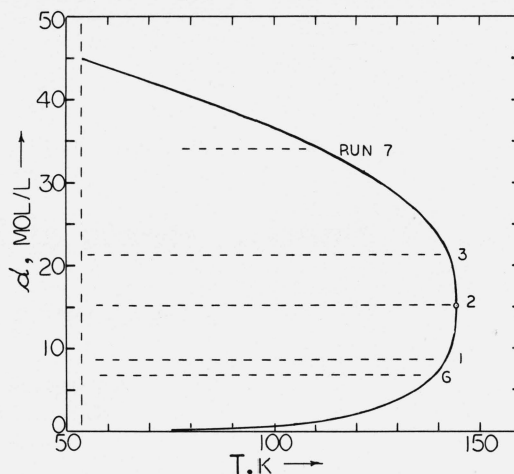


FIGURE 2. Locus of two-phase specific heat measurements.

TABLE 1. Loading conditions for the samples

| Run | T, K | P, Atm | P, MN/m ² | V, cm ³ | D, Mol/l | N, Mol |
|--------|---------|---------|----------------------|--------------------|----------|--------|
| 1..... | 174.825 | 83.142 | 8.4244 | 73.014 | 8.709 | 0.6360 |
| 2..... | 166.789 | 102.908 | 10.4272 | 73.008 | 15.184 | 1.1087 |
| 3..... | 175.609 | 183.593 | 18.6026 | 73.114 | 21.245 | 1.5535 |
| 6..... | 195.075 | 85.469 | 8.6601 | 73.079 | 6.770 | 0.4948 |
| 7..... | 116.282 | 87.461 | 8.8620 | 72.850 | 34.098 | 2.4843 |

both the direct and derived results for these two-phase specific heat measurements. The pressure and the densities of vapor and of liquid are computed by formulas in the appendix. The first column of table 2 gives the experimental run (sequence) followed by two digits for the individual measurement at this density. Next is the average temperature in the interval and the bomb volume derived from the pressure at this average temperature. The fourth column gives overall density, ρ_{av} . Following columns give the calorimetric temperature increment, ΔT ; the experimental gross heat capacity prior to any adjustments, $Q/\Delta T$; the tare heat capacity; the specific heat, \bar{C}_v , of the two-phase sample; the derived specific heat, C_σ , of liquid along the coexistence path; and finally the estimated uncertainties (errors) in these specific heats, calculated as described in [3].

Figure 3 shows the two-phase specific heat data for our first three runs, plotted in coordinates \bar{C}_v/T versus T . This plot has been used for interpolation of \bar{C}_v/T onto isotherms, useful to derive values for d^2P/dT^2 via the thermodynamic relation,

$$\bar{C}_v/T = -d^2G/dT^2 + [d^2P/dT^2]/\rho. \quad (3)$$

Results in table 3 are compared with values from the vapor pressure equation of the appendix.

Specific heat of liquid along the coexistence path is derived by the relation [7]

$$C_\sigma = \bar{C}_v - \frac{T_a}{\rho} \left\{ \frac{1}{\rho} \frac{d\rho}{dT} \frac{dP}{dT} + \left[\frac{\rho \cdot V_b}{N_b} - 1 \right] \frac{d^2P}{dT^2} \right\}. \quad (4)$$

TABLE 2. *Specific heats of fluorine at coexistence*

| ID | Temp. deg. K | V , bmb cm ³ | D , avr mol/l | ΔT deg. K | $Q/\Delta T$ J/deg. | Tare J/deg. | \bar{C}_v J/M-K | C_σ J/M-K | Errors, percent | |
|----------|-----------------|------------------------------|--------------------|----------------------|------------------------|----------------|----------------------|---------------------|-----------------|------------|
| | | | | | | | | | \bar{C}_v | C_σ |
| 101..... | 56.998 | 72.669 | 8.752 | 2.682 | 58.930 | 24.237 | 54.550 | 54.309 | 0.48 | 0.48 |
| 102..... | 60.751 | 72.673 | 8.751 | 4.825 | 62.028 | 26.340 | 56.116 | 55.618 | .41 | .42 |
| 103..... | 66.124 | 72.679 | 8.751 | 5.923 | 66.399 | 29.866 | 57.444 | 56.279 | .41 | .43 |
| 104..... | 72.184 | 72.688 | 8.749 | 6.208 | 71.556 | 33.916 | 59.183 | 56.700 | .42 | .45 |
| 105..... | 78.516 | 72.698 | 8.748 | 6.472 | 77.238 | 37.960 | 61.758 | 57.140 | .42 | .49 |
| 106..... | 85.115 | 72.710 | 8.747 | 6.725 | 83.556 | 41.886 | 65.519 | 57.820 | .43 | .54 |
| 107..... | 91.892 | 72.724 | 8.745 | 6.849 | 90.363 | 45.593 | 70.388 | 58.689 | .43 | .60 |
| 108..... | 98.944 | 72.740 | 8.743 | 6.932 | 97.859 | 49.108 | 76.643 | 60.040 | .42 | .66 |
| 109..... | 105.907 | 72.757 | 8.741 | 7.029 | 105.644 | 52.253 | 83.930 | 61.940 | .42 | .73 |
| 110..... | 112.955 | 72.777 | 8.739 | 7.093 | 113.841 | 55.131 | 92.244 | 64.475 | .41 | .80 |
| 111..... | 120.087 | 72.799 | 8.736 | 7.215 | 122.778 | 57.759 | 102.096 | 68.441 | .40 | .86 |
| 112..... | 126.982 | 72.823 | 8.733 | 6.677 | 132.505 | 60.054 | 113.716 | 74.905 | .40 | .91 |
| 113..... | 133.380 | 72.847 | 8.730 | 6.167 | 143.436 | 61.992 | 127.764 | 86.239 | .40 | .94 |
| 114..... | 137.922 | 72.866 | 8.728 | 2.974 | 152.921 | 63.267 | 140.725 | 102.443 | .46 | 1.04 |
| | | | | | | | | | | |
| 201..... | 57.538 | 72.669 | 15.257 | 4.551 | 85.452 | 24.502 | 54.975 | 54.850 | .37 | .37 |
| 202..... | 62.557 | 72.675 | 15.255 | 5.496 | 89.647 | 27.492 | 56.062 | 55.749 | .36 | .36 |
| 203..... | 68.562 | 72.683 | 15.254 | 6.522 | 94.650 | 31.506 | 56.953 | 56.211 | .36 | .37 |
| 204..... | 75.531 | 72.693 | 15.252 | 7.428 | 100.628 | 36.086 | 58.214 | 56.622 | .36 | .38 |
| 205..... | 84.071 | 72.708 | 15.248 | 9.668 | 108.467 | 41.285 | 60.595 | 57.409 | .35 | .40 |
| 206..... | 93.327 | 72.727 | 15.244 | 8.854 | 117.344 | 46.337 | 64.043 | 58.563 | .36 | .45 |
| 207..... | 101.874 | 72.747 | 15.240 | 8.260 | 126.022 | 50.470 | 68.137 | 60.259 | .37 | .49 |
| 208..... | 109.854 | 72.768 | 15.236 | 7.724 | 134.658 | 53.901 | 72.824 | 62.765 | .37 | .53 |
| 209..... | 117.335 | 72.790 | 15.231 | 7.253 | 143.307 | 56.777 | 78.021 | 66.354 | .37 | .57 |
| 210..... | 125.182 | 72.816 | 15.226 | 5.493 | 153.127 | 59.476 | 84.391 | 72.317 | .39 | .62 |
| 211..... | 130.632 | 72.836 | 15.221 | 5.438 | 161.284 | 61.181 | 90.114 | 79.755 | .39 | .63 |
| 212..... | 135.869 | 72.857 | 15.217 | 5.076 | 171.190 | 62.700 | 97.572 | 93.541 | .39 | .64 |
| 213..... | 140.687 | 72.878 | 15.212 | 4.653 | 186.562 | 64.005 | 109.849 | 130.404 | .38 | .62 |
| 214..... | 143.436 | 72.890 | 15.210 | 0.904 | 204.756 | 64.712 | 125.623 | 256.445 | .70 | .75 |
| | | | | | | | | | | |
| 301..... | 55.173 | 72.667 | 21.378 | 2.729 | 107.984 | 23.496 | 54.386 | 54.343 | .39 | .40 |
| 302..... | 57.860 | 72.670 | 21.377 | 2.654 | 110.311 | 24.667 | 55.130 | 55.055 | .40 | .40 |
| 303..... | 61.376 | 72.674 | 21.376 | 4.386 | 113.341 | 26.733 | 55.751 | 55.608 | .36 | .36 |
| 304..... | 66.187 | 72.679 | 21.375 | 5.244 | 117.404 | 29.908 | 56.322 | 56.025 | .35 | .35 |
| 305..... | 71.829 | 72.687 | 21.372 | 6.047 | 122.139 | 33.683 | 56.940 | 56.350 | .35 | .36 |
| 306..... | 78.281 | 72.698 | 21.369 | 6.865 | 127.752 | 37.815 | 57.893 | 56.809 | .34 | .36 |
| 307..... | 84.987 | 72.710 | 21.366 | 6.562 | 133.702 | 41.813 | 59.149 | 57.394 | .35 | .38 |
| 308..... | 91.937 | 72.724 | 21.361 | 7.356 | 140.093 | 45.617 | 60.813 | 58.257 | .35 | .40 |
| 309..... | 99.435 | 72.741 | 21.356 | 7.659 | 147.276 | 49.341 | 63.037 | 59.622 | .35 | .42 |
| 310..... | 107.126 | 72.761 | 21.351 | 7.741 | 154.930 | 52.772 | 65.734 | 61.643 | .35 | .44 |
| 311..... | 114.649 | 72.782 | 21.344 | 7.325 | 162.713 | 55.780 | 68.799 | 64.563 | .35 | .46 |
| 312..... | 121.502 | 72.804 | 21.338 | 6.996 | 170.708 | 58.249 | 72.339 | 68.925 | .36 | .48 |
| 313..... | 128.311 | 72.827 | 21.331 | 6.653 | 179.334 | 60.471 | 76.422 | 75.868 | .36 | .49 |
| 314..... | 133.951 | 72.849 | 21.324 | 4.659 | 188.464 | 62.157 | 81.180 | 87.061 | .38 | .52 |
| 315..... | 138.484 | 72.868 | 21.319 | 4.443 | 198.904 | 63.419 | 86.861 | 107.109 | .38 | .52 |
| | | | | | | | | | | |
| 601..... | 57.905 | 72.670 | 6.810 | 7.348 | 51.665 | 24.691 | 54.510 | 54.116 | .41 | .41 |
| 602..... | 64.890 | 72.678 | 6.809 | 6.635 | 57.346 | 29.037 | 57.209 | 55.883 | .43 | .45 |
| 603..... | 72.088 | 72.688 | 6.808 | 7.771 | 63.442 | 33.854 | 59.791 | 56.442 | .43 | .48 |
| 604..... | 79.891 | 72.701 | 6.807 | 7.852 | 70.512 | 38.803 | 64.075 | 56.976 | .44 | .55 |
| 605..... | 87.709 | 72.715 | 6.805 | 7.802 | 78.174 | 43.344 | 70.382 | 57.829 | .45 | .63 |
| 606..... | 95.511 | 72.732 | 6.804 | 7.834 | 86.323 | 47.440 | 78.536 | 59.015 | .44 | .73 |
| 607..... | 103.310 | 72.751 | 6.802 | 7.838 | 94.932 | 51.117 | 88.481 | 60.760 | .44 | .83 |
| 608..... | 111.099 | 72.772 | 6.800 | 7.774 | 104.070 | 54.402 | 100.274 | 63.435 | .43 | .93 |
| 609..... | 118.847 | 72.795 | 6.798 | 7.752 | 113.803 | 57.321 | 113.982 | 67.447 | .42 | 1.02 |
| 610..... | 126.540 | 72.821 | 6.795 | 7.669 | 124.691 | 59.913 | 130.613 | 74.274 | .41 | 1.10 |
| 611..... | 133.839 | 72.849 | 6.792 | 6.960 | 137.309 | 62.124 | 151.266 | 86.946 | .40 | 1.14 |
| | | | | | | | | | | |
| 701..... | 77.842 | 72.697 | 34.173 | 2.136 | 179.095 | 37.542 | 56.979 | 56.793 | .42 | .43 |
| 702..... | 80.589 | 72.702 | 34.170 | 3.358 | 181.333 | 39.227 | 57.202 | 56.992 | .37 | .38 |
| 703..... | 84.641 | 72.709 | 34.167 | 4.745 | 184.786 | 41.614 | 57.631 | 57.402 | .35 | .36 |
| 704..... | 89.737 | 72.719 | 34.162 | 5.447 | 189.068 | 44.450 | 58.212 | 58.005 | .34 | .36 |
| 705..... | 95.545 | 72.732 | 34.156 | 6.172 | 193.931 | 47.457 | 58.959 | 58.882 | .34 | .36 |
| 706..... | 101.200 | 72.745 | 34.150 | 5.147 | 198.700 | 50.162 | 59.788 | 60.008 | .35 | .38 |
| 707..... | 106.285 | 72.758 | 34.144 | 5.033 | 203.295 | 52.415 | 60.729 | 61.434 | .35 | .38 |

TABLE 3. Comparisons d^2P/dT^2 for fluorine

| T, K | $\bar{C}_v/T = -d^2G/dT^2 + (d^2P/dT^2) \cdot v$ | |
|----------|--|----------------|
| | d^2P/dT^2 , atm/K ² | |
| | Expt'l. \bar{C}_v/T | V.P. eq. (5.3) |
| 80..... | 0.0080 \pm 0.0008 | 0.0073 |
| 90..... | .0140 .0008 | .0133 |
| 100..... | .0212 .0008 | .0203 |
| 110..... | .0289 .0008 | .0280 |
| 120..... | .0371 .0008 | .0363 |
| 130..... | .0475 .0009 | .0464 |
| 140..... | .063 .0035 | .0647 |

Figure 4 shows C_σ for the liquid on this path. On the scale of this plot the data appear to be linear in temperatures below the boiling point (85 K). Figure 5 examines behavior of the data as $T \rightarrow T_c$. Upon subtracting C_v^0 , we obtain a nearly linear plot in the logarithmic coordinates of figure 5, corresponding to

$$C_\sigma \sim C_v^0 + \text{const} \cdot (1 - T/T_c)^{-\epsilon} \quad (5)$$

where the exponent is roughly $\epsilon = 0.5$.

4. Analytical Representation of C_σ

For thermal computations along the coexistence path we need a description of $C_\sigma(T)$. It is convenient

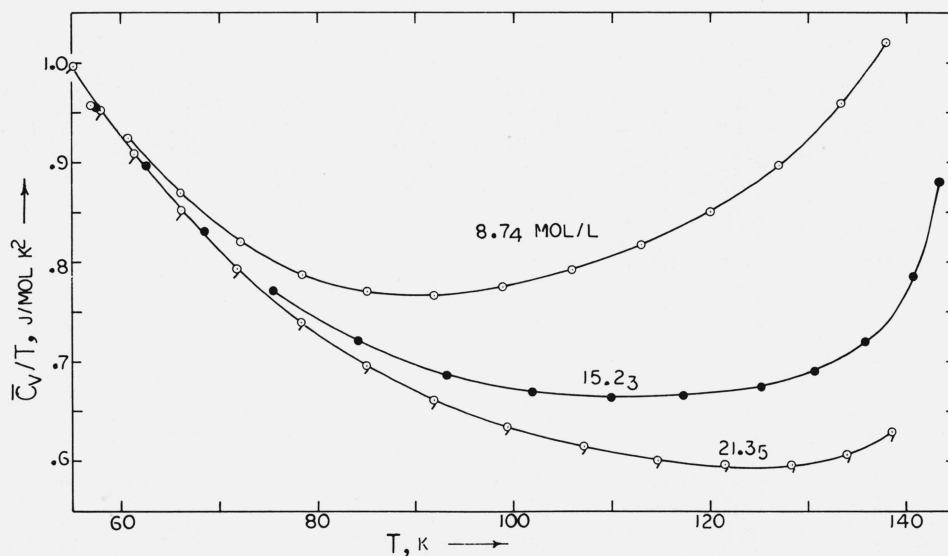


FIGURE 3. Two-phase specific heats of fluorine at constant volume.

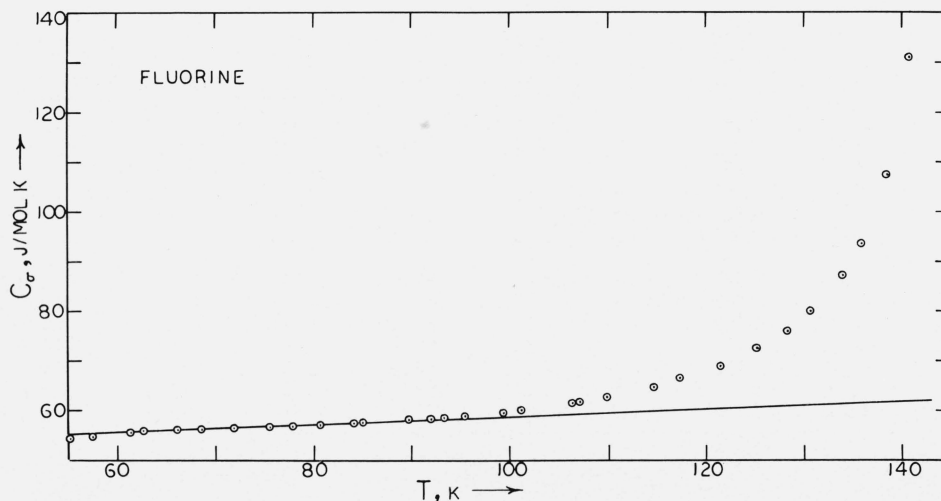


FIGURE 4. Derived specific heats of liquid fluorine along the coexistence path.

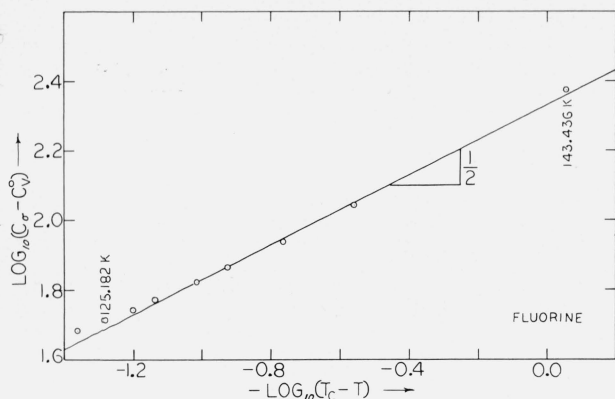


FIGURE 5. Residual specific heat: $(C_\sigma - C_\sigma^0)$, J/mol K, versus $(T_c - T)$ in log-log coordinates.

to define a reduced independent variable which is zero at the critical point, $x \equiv (1 - T/T_c)$. We have sought a simpler form than was used for oxygen. The following expression,

$$C_\sigma = A_1/x^\epsilon + \sum_{i=2}^N A_i x^{i-2}, \quad (6)$$

is sufficient for oxygen with $N = 3$ terms only, giving an rms relative deviation of 0.33 percent for the 86 data in [3]. For the present fluorine data, however, we must take $N = 6$ terms for optimum representation, $\epsilon = 0.593$,

$$\begin{aligned} A_1 &= 10.76 \ 214 & A_4 &= -148.92 \ 825 \\ A_2 &= 33.88 \ 593 & A_5 &= 341.88 \ 386 \\ A_3 &= 34.85 \ 555 & A_6 &= -265.99 \ 546 \end{aligned}$$

Table 4 compares the data used for C_σ with values calculated from (6). There is a systematic difference of roughly 0.1 percent between different runs. This increases as the amount of sample (density) decreases. For this reason, runs at densities below critical were omitted in deriving constants for the fitting function. The rms relative deviation of 0.11 percent for (6) with the remaining data is smaller than the uncertainty of individual points. Figure 6 shows low-temperature behavior of the C_σ data relative to the calculated line.

A few specific heats have been reported previously for fluorine in the condensed phase at $T < 85$ K, [8,9]. No clear description of the experimental conditions was given. The data in [9] are labeled C_p , and previous reports mention recording the pressure before and after each heating period [10]. The reported values in table 5 are compared with our calculated values from (6) for liquid on the coexistence path.

TABLE 4. Derived and calculated values of C_σ , J/mol K

| ID | T, K | Csat | Calc | Percent |
|----------|---------|---------|---------|---------|
| 301..... | 53.481 | 54.343 | 54.489 | |
| | 54.000 | | 54.578 | |
| | 55.173 | | 54.766 | |
| | 56.000 | | 54.890 | |
| 201..... | 57.538 | 54.850 | 55.104 | |
| 302..... | 57.860 | 55.055 | 55.147 | -0.17 |
| 303..... | 61.376 | 55.608 | 55.554 | .10 |
| 202..... | 62.557 | 55.749 | 55.672 | .14 |
| 304..... | 66.187 | 56.025 | 55.991 | .06 |
| 203..... | 68.562 | 56.211 | 56.172 | .07 |
| 305..... | 71.829 | 56.350 | 56.403 | -.09 |
| 204..... | 75.531 | 56.622 | 56.658 | -.06 |
| 701..... | 77.842 | 56.793 | 56.824 | -.05 |
| 306..... | 78.281 | 56.809 | 56.857 | -.08 |
| 702..... | 80.589 | 56.992 | 57.037 | -.08 |
| 205..... | 84.071 | 57.409 | 57.344 | .11 |
| 703..... | 84.641 | 57.402 | 57.399 | .01 |
| 307..... | 84.987 | 57.394 | 57.433 | -.07 |
| 704..... | 89.737 | 58.005 | 57.976 | .05 |
| 308..... | 91.937 | 58.257 | 58.279 | -.04 |
| 206..... | 93.327 | 58.563 | 58.490 | .13 |
| 705..... | 95.545 | 58.882 | 58.861 | .04 |
| 309..... | 99.435 | 59.622 | 59.631 | -.01 |
| 706..... | 101.200 | 60.008 | 60.036 | -.05 |
| 207..... | 101.874 | 60.259 | 60.201 | .10 |
| 707..... | 106.285 | 61.434 | 61.437 | -.00 |
| 310..... | 107.126 | 61.643 | 61.707 | -.10 |
| 208..... | 109.854 | 62.765 | 62.670 | .15 |
| 311..... | 114.649 | 64.563 | 64.754 | -.29 |
| 209..... | 117.335 | 66.354 | 66.200 | .23 |
| 312..... | 121.502 | 68.925 | 68.996 | -.10 |
| 210..... | 121.182 | 72.317 | 72.276 | .06 |
| 313..... | 128.311 | 75.868 | 76.004 | -.18 |
| 211..... | 130.632 | 79.755 | 79.642 | .14 |
| 314..... | 133.951 | 87.061 | 87.059 | .00 |
| 212..... | 135.869 | 93.541 | 93.425 | .12 |
| 315..... | 138.484 | 107.109 | 107.265 | -.15 |
| 213..... | 140.687 | 130.404 | 130.355 | .04 |
| 214..... | 143.436 | 256.445 | 256.446 | -.00 |

NP = 34, RMSPECT = 0.112

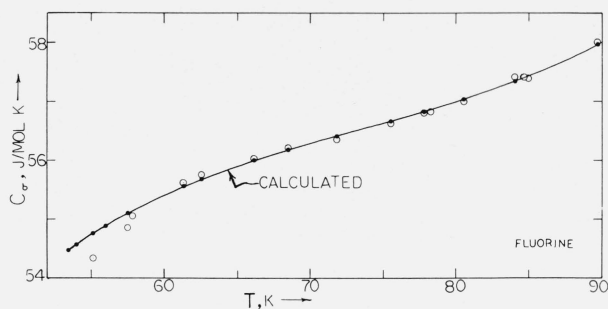


FIGURE 6. Behavior of C_σ data at low temperatures.

5. Appendixes

5.1. Resistance Thermometer Formula

Coefficients for eq 5.1 were obtained by least squares. Data are from NBS calibration tables on the

TABLE 5. Other specific heats for the condensed phase, J/mol K

| T, K | C _x , unknown conditions | | C _σ Eq (6) |
|------------|-------------------------------------|---------------|--------------------------|
| | Kanda [8] | Hu et al. [9] | |
| 57.50..... | 45.4 | | 55.1 |
| 58.14..... | | 57.3 | 55.2 |
| 62.27..... | | 57.3 | 55.6 |
| 62.51..... | 45.7 | | 55.7 |
| 67.05..... | | 56.7 | 56.1 |
| 67.49..... | 45.9 | | 56.1 |
| 71.86..... | | 56.8 | 56.4 |
| 76.60..... | | 57.4 | 56.7 |
| 77.10..... | 46.5 | | 56.8 |
| 81.32..... | | 57.7 | 57.1 |
| 83.41..... | 46.9 | | 57.3 |

IPTS (1968) for platinum thermometer L.N.1,506,157. Maximum deviations are 4 parts per million (0.14 mK) in the range $20 \leq T \leq 100$ K, and 6 parts per million (1.95 mK) in the range $100 \leq T \leq 600$ K. Variables for (5.1) include $x \equiv R/R_1$ where R is thermometer resistance and R_1 is a constant to be found; $T_0 \equiv 273.15$ K; $u \equiv \log_e(1+x)$; and $w \equiv \log_e(1+1/x)$,

$$T/T_0 = A_1 + A_2 \cdot x + A_3 \cdot u + A_4 \cdot x \cdot u + x \cdot \sum_{i=5}^{17} A_i \cdot w^{i-3}. \quad (5.1)$$

Table 5.1-A gives the constants for (5.1). The number of figures in each is based on the maximum value of each term in (5.1). Table 5.1-B gives a selection of data and calculated values for T and for the first derivative, dT/dR .

TABLE 5.1-A. Constants for resistance thermometer

| |
|--|
| $R_1 = 13.0$ ohm |
| $A_1 = -1.0874$ 7037 . . . $\times 10^1$ |
| $A_2 = -2.6699$ 4012 . . . $\times 10^0$ |
| $A_3 = 9.2443$ 2475 . . . $\times 10^0$ |
| $A_4 = 7.9896$ 2549 . . . $\times 10^{-1}$ |
| $A_5 = 2.0807$ 0866 . . . $\times 10^1$ |
| $A_6 = -1.8099$ 5755 . . . $\times 10^1$ |
| $A_7 = 2.2519$ 8377 2 . . . $\times 10^1$ |
| $A_8 = -1.9086$ 9836 9 4 . $\times 10^1$ |
| $A_9 = 1.2724$ 9642 9 9 . $\times 10^1$ |
| $A_{10} = -6.3571$ 7850 4 7 0 $\times 10^0$ |
| $A_{11} = 2.3872$ 5690 3 4 4 $\times 10^0$ |
| $A_{12} = -6.6558$ 6282 7 2 7 $\times 10^{-1}$ |
| $A_{13} = 1.3550$ 6466 3 3 4 $\times 10^{-1}$ |
| $A_{14} = -1.9527$ 0069 5 7 9 $\times 10^{-2}$ |
| $A_{15} = 1.8847$ 0886 4 3 . $\times 10^{-3}$ |
| $A_{16} = -1.0919$ 0062 3 0 . $\times 10^{-4}$ |
| $A_{17} = 2.8697$ 1011 5 . . $\times 10^{-6}$ |

5.2. Tare Heat Capacity C_b of the Empty Calorimeter

These heat capacities were measured by procedures identical with those used when the calorimeter contained fluid. Results are given here to show the precision attainable in absence of contained fluid. We

TABLE 5.1-B. Resistance thermometer comparisons

| R, ohm | Temperature, K | | DT/DR, K/ohm | |
|----------|----------------|-----------|--------------|--------|
| | Data | Calcd | Data | Calcd |
| 0.10822 | 20 | 20.00000 | 54.450 | 53.996 |
| .15046 | 22 | 22.00001 | 42.220 | 41.960 |
| .20387 | 24 | 24.00010 | 33.910 | 33.744 |
| .26917 | 26 | 25.99998 | 28.140 | 28.013 |
| .43669 | 30 | 29.99999 | 20.870 | 20.802 |
| .71483 | 35 | 34.99999 | 15.920 | 15.886 |
| 1.06277 | 40 | 39.99994 | 13.210 | 13.188 |
| 1.92143 | 50 | 50.00002 | 10.610 | 10.600 |
| 2.92121 | 60 | 60.00002 | 9.580 | 9.576 |
| 3.99152 | 70 | 69.99999 | 9.180 | 9.177 |
| 5.09086 | 80 | 80.00004 | 9.040 | 9.045 |
| 6.19807 | 90 | 89.99990 | 9.030 | 9.032 |
| 7.30315 | 100 | 100.00003 | 9.069 | 9.072 |
| 9.49254 | 120 | 120.00031 | 9.199 | 9.202 |
| 11.65079 | 140 | 139.99974 | 9.326 | 9.328 |
| 13.78232 | 160 | 159.99946 | 9.431 | 9.434 |
| 15.89232 | 180 | 180.00029 | 9.519 | 9.522 |
| 17.98437 | 200 | 200.00103 | 9.596 | 9.597 |
| 20.57753 | 225 | 225.00024 | 9.681 | 9.682 |
| 23.14885 | 250 | 249.99855 | 9.760 | 9.761 |
| 25.49666 | 273 | 272.99897 | 9.830 | 9.832 |
| 28.23168 | 300 | 300.00079 | 9.911 | 9.914 |
| 30.74399 | 325 | 325.00188 | 9.988 | 9.989 |
| 33.23712 | 350 | 350.00185 | 10.065 | 10.066 |
| 35.51399 | 373 | 373.00105 | 10.136 | 10.137 |
| 38.16643 | 400 | 399.99978 | 10.220 | 10.221 |
| 43.02058 | 450 | 449.99831 | 10.379 | 10.380 |
| 47.80024 | 500 | 499.99964 | 10.541 | 10.543 |
| 52.50580 | 550 | 550.00194 | 10.708 | 10.710 |
| 57.13738 | 600 | 599.99805 | 10.881 | 10.880 |

express C_b in J/K, and describe the data by use of argument $x \equiv 100/T$,

$$\log_e(C_b/50) = \sum_{i=0}^7 C_i \cdot x^i, \quad (5.2)$$

| | |
|---------------------|---------------------|
| $C_0 = 0.834$ 3170 | $C_4 = -0.617$ 8472 |
| $C_1 = -1.254$ 9634 | $C_5 = 1.434$ 6722 |
| $C_2 = 1.404$ 5656 | $C_6 = -0.792$ 6938 |
| $C_3 = -1.167$ 3943 | $C_7 = 0.151$ 4253. |

Experimental and calculated values for C_b are compared in table 5.2.

5.3. The Vapor Pressure of Fluorine

The equation from [11] uses argument $x \equiv (1 - T_i/T)/(1 - T_i/T_c)$,

$$\log_e(P/P_t) = A_1 \cdot x + A_2 \cdot x^2 + A_3 \cdot x^3 + A_4 \cdot x \cdot (1-x)^6. \quad (5.3)$$

Constants are reported in [2],

| | |
|--------------------------------|----------------------|
| $P_t = 252.0$ N/m ² | $A_1 = 7.8959$ 2346 |
| $T_t = 53.4811$ K | $A_2 = 3.3876$ 5063 |
| $T_c = 144.31$ K | $A_3 = -1.3459$ 0196 |
| $\epsilon = 1.4327$ | $A_4 = 2.7313$ 8936. |

TABLE 5.2. Experimental and calculated C_b , J/K

| T_{av} , K | ΔT | C_b , J/K | Calc | Percent |
|--------------|------------|-------------|--------|---------|
| 58.263 | 5.540 | 24.881 | 24.882 | -0.003 |
| 63.565 | 5.132 | 28.160 | 28.154 | .021 |
| 68.400 | 4.569 | 31.382 | 31.397 | -.050 |
| 73.178 | 5.016 | 34.579 | 34.567 | .035 |
| 78.403 | 5.458 | 37.895 | 37.891 | .011 |
| 84.151 | 6.067 | 41.330 | 41.332 | -.003 |
| 89.961 | 5.590 | 44.566 | 44.570 | -.008 |
| 95.780 | 6.119 | 47.565 | 47.573 | -.017 |
| 102.108 | 6.573 | 50.582 | 50.576 | .012 |
| 108.805 | 6.860 | 53.463 | 53.473 | -.018 |
| 115.658 | 6.896 | 56.174 | 56.159 | .025 |
| 122.840 | 7.515 | 58.689 | 58.703 | -.024 |
| 130.592 | 8.055 | 61.212 | 61.169 | .070 |
| 130.114 | 8.062 | 61.016 | 61.024 | -.014 |
| 138.297 | 8.378 | 63.352 | 63.368 | -.026 |
| 146.798 | 8.738 | 65.541 | 65.543 | -.004 |
| 155.637 | 9.048 | 67.559 | 67.564 | -.007 |
| 164.902 | 9.637 | 69.436 | 69.459 | -.033 |
| 174.769 | 10.274 | 71.283 | 71.266 | .024 |
| 185.191 | 11.128 | 72.984 | 72.976 | .011 |
| 196.516 | 11.765 | 74.625 | 74.643 | -.024 |
| 208.533 | 12.559 | 76.271 | 76.229 | .054 |
| 221.291 | 13.273 | 77.739 | 77.745 | -.007 |
| 234.509 | 13.536 | 79.123 | 79.162 | -.050 |
| 247.911 | 13.702 | 80.442 | 80.467 | -.031 |
| 254.509 | 13.782 | 81.091 | 81.068 | .029 |
| 268.123 | 13.965 | 82.256 | 82.230 | .033 |
| 282.114 | 14.621 | 83.338 | 83.329 | .011 |
| 296.823 | 15.517 | 84.378 | 84.395 | -.020 |

NP = 29, RMSPCT = 0.028

5.4. The Vapor Density ρ_g of Fluorine

The equation for saturated vapor [12] uses arguments $x \equiv T/T_c$ and $z \equiv (1-x)$,

$$\log_e(\rho_g/\rho_c) = A_1 \cdot (1-1/x) + A_2 \cdot z^{0.35} + \sum_{i=3}^7 A_i \cdot z^{i-2}. \quad (5.4)$$

Constants are reported in [2],

$$\begin{aligned} \rho_c &= 15.10 \text{ mol/liter} & A_3 &= -0.1880 \ 6690 \\ T_c &= 144.31 \text{ K} & A_4 &= 6.2116 \ 5939 \\ A_1 &= 4.8554 \ 7085 & A_5 &= -22.9600 \ 8970 \\ A_2 &= -1.9601 \ 5519 & A_6 &= 46.9524 \ 6230 \\ & & A_7 &= -43.0650 \ 2700 \end{aligned}$$

5.5. The Liquid Density ρ_l of Fluorine

The saturated liquid densities are described in [2] with the same arguments as in section 5.4 above,

$$\rho_l/\rho_c = 1 + A_0 \cdot z^{0.35} + \sum_{i=1}^5 A_i \cdot z^i, \quad (5.5)$$

$$\begin{aligned} A_0 &= 1.8188 \ 1076 & A_3 &= 1.3728 \ 4761 \\ A_1 &= 0.8752 \ 3649 & A_4 &= -1.0133 \ 1503 \\ A_2 &= -0.8504 \ 5891 & A_5 &= 0.2738 \ 4013. \end{aligned}$$

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